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Canada Centre for Mineral and Energy Technology | Centre canadien de la technologie des minéraux et de l'énergie

THE DIRECT CONVERSION OF METHANE TO METHANOL BY CONTROLLED OXIDATION

"A REVIEW"

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ENERGY RESEARCH PROGRAM
ENERGY RESEARCH LABORATORIES
DIVISION REPORT ERP/ERL 83-16 (TR)

AUG 19 1983
MICROMEDIA

31pp

ABSTRACT

Substantial reserves of natural gas in Canada provide sufficient incentive to develop new processes for its direct conversion to liquid fuels. One such process is the controlled oxidation of methane (major component in natural gas) to methanol. If its commercial viability is proven it could replace the existing less efficient two stage process, involving the steam reforming of natural gas to synthesis gas ($CO+H_2$) and its subsequent conversion to methanol.

A literature review of the past work related to direct oxidation of methane to methanol is reported. Process conditions most conducive to high methanol yield are discussed. Finally, suggestions are made for future research in this field.

RÉSUMÉ

Il existe, au Canada, des réserves substantielles de gaz naturel qui constituent des facteurs stimulants suffisamment importants pour que l'on mette au point de nouveaux procédés de conversion directe du gaz en combustibles liquides. Un de ces procédés consiste à contrôler l'oxydation du méthane (principal composant du gaz naturel) en méthanol. Si on arrive à prouver la rentabilité commerciale de ce procédé, celui-ci pourrait remplacer le procédé en deux étapes qui est beaucoup moins rentable et qui implique la transformation du gaz naturel en gaz de synthèse ($CO+H_2$) puis le transformation du gaz de synthèse en méthanol.

On fait rapport de l'analyse de documentation des travaux précédents effectués sur l'oxydation directe du méthane en méthanol. On discute des conditions des procédés qui fournissent le plus haut rendement de méthanol. En dernier lieu, on fait des suggestions en vue de recherches futures dans ce domaine.

CONTENTS

	Page
ABSTRACT	i
SUMMAIRE	ii
INTRODUCTION	1
WORK DONE IN THE PAST	3
Effect of temperature, presure, oxygen concentration and residence time	13
Effect of catalysts and presence of higher hydrocarbons	13
NEED FOR FUTURE WORK	14
REFERENCES	15-21

TABLES

No.		
1.	The effect of temperature upon the survival of methyl alcohol and formaldehyde in the products of methane oxidation at high pressure	22
2.	Yield of methanol and formaldehyde from the oxidations of methane in a flow system at 50 atm	23
3.	Experiments at a pressure of 185 atm. showing the effect of temperature, rate of flow and oxygen concentration on methanol yields	24
4.	Summary of methane to methanol conversion	25

FIGURES

1.	Methanol yield as a function of pressure and oxygen concentration...	26
2.	Methanol conversion as a function pressure	26
3.	Methanol conversion as a function of oxygen concentration	26
4.	Yield of products as a function of compression ratio	27
5.	Yield of (1) C_2H_6 (2) C_2H_4 (3) C_2H_2 and (4) C_3M_6 x 10 as a function of compression ratio	27
6.	Yield of (1) CO and (2) H_2 as a function of compression ratio	27

INTRODUCTION

Although Canada is a net exporter of energy, 25 percent of its petroleum crude requirement is imported. This peculiar situation exposes Canada to economic and political pressures that it need not endure. One simple way to achieve self-sufficiency in energy would be to increase the domestic consumption of fuels which are now exported. Such a shift in resource utilization is easier said than done because of the problems related to the infrastructure of fuel usage and distribution. The most relevant case is that of finding a suitable substitute for gasoline in the transportation sector.

Sustained efforts are being made in many parts of the World to find a substitute for gasoline as transportation fuel. Gasoline-alcohol blends (gasohols) have been introduced in many countries including the United States and neat alcohols are also being used, primarily in Brazil, as substitutes for gasoline. Propane, liquified at 10 atmospheres in cylinders, and compressed natural gas at 200 atmospheres are also being used as transportation fuels in Canada. Among all these gasoline substitution candidates, methanol has certain advantages as a liquid fuel and can be manufactured from a variety of raw materials such as natural gas, coal, municipal solid waste, animal refuse and biomass. At present almost all of the methanol produced in Canada comes from natural gas via a two stage process (reforming to synthesis gas and catalytic conversion of syngas).

The existing commercial process for the production of methanol from natural gas (essentially methane) involves the intermediate formation of synthesis gas.

$$CH_4(g) + H_2O(g) \xrightarrow[\text{heat}]{[Ni]} CO(g) + 3H_2(g) \quad \Delta H^\circ = 49.3 \text{ kcal} \quad (1)$$

The "synthesis gas" is then converted by a catalytic process, after appropriate balancing for CO and H_2 (the excess H_2 is used to generate the steam required in Reaction (1)), into methanol.

$$CO(g) + 2H_2(g) \xrightarrow[50\text{-}100 \text{ atm}]{\text{catalyst}} CH_3OH(g) \qquad \Delta H^\circ = -21.7 \text{ kcal} \quad (2)$$

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A recent description of the overall process using either natural gas or coal as a starting material has been presented by Piquette (1). This process suffers from the requirement of complicated engineering steps and also from the relative inefficiency of carrying out extensive oxidation of methane to carbon monoxide and then reduction of carbon monoxide to methanol. In addition, the "synthesis gas" must be clean, free from sulfur, chloride and other catalyst poisons. The overall efficiency of a 2000 tonne/day plant is expected to be about 70% for fuel grade methanol provided that the excess steam produced can be utilized on site or sold.

Clearly a direct conversion of methane to methanol, where the oxidation process is intercepted at the stage of initial oxidation, not only yields a liquid product in one step but is also preferred because it will be energetically more efficient.

$$CH_4(g) + 1/2\ O_2(g) \longrightarrow CH_3OH(1) \qquad \Delta H^\circ = -30.7 \text{ kcal} \qquad (3)$$

The recent demand for methanol as a fuel and a starting material for many industrial processes has suggested (2) that new technology must be developed for the commercial production of methanol.

For Canada with its substantial reserves of natural gas at remote locations such as the Beaufort Sea, a single step conversion process of methane to methanol will have far reaching economic implications.

This paper reviews the research which has been concerned with the conversion of methane to methanol and also carefully examines the process conditions which are most conducive to the direct oxidation process.

..../3

WORK DONE IN THE PAST

The oxidation of hydrocarbons in general, and methane in particular has been studied for over a century. The kinetics and mechanism for the oxidation reaction have been elucidated for the complete combustion of methane to carbon dioxide and water. The intermediate products, hydrogen, carbon monoxide, formaldehyde and formic acid, were identified by 1903. Despite many efforts, no evidence of methanol as an intermediate product was found until the reaction was carried out at high pressures (3 to 12).

In 1932 Newitt and Haffner (8) reported the formation of methanol in the high pressure oxidation of methane. These authors also reported that formaldehyde and formic acid were produced as condensible products. They were not able to detect the presence of peroxides. Under Newitt and Haffner's conditions, the maximum yield of methanol was about 22% of the methane consumed. The maximum methanol to formaldehyde ratio was 40. The reaction was carried out in a static system at temperatures from 360° to 393°C and pressures of 50 to 150 atm. The reaction time vaied from one to 100 minutes in the presence of either excess methane or inert gases such as nitrogen, carbon dioxide and water. Some typical results reported by Newitt and Haffner are given in Table 1.

The high pressure partial oxidation of methane to methanol was studied independently by Pichler and Reder (9) under both static and flow conditions. In the static experiments the pressure was varied up to a maximum of 160 atm and in the flow system pressures up to 100 atm were used. Under static conditions of 160 atm and 350°C, the yield of methanol was a maximum (14.8% of the methane consumed) when the oxygen content was at 10%. Under flow conditions at 100 atm and 500°C with a reaction time of 10 secs in a 4 mm porcelain lined capillary reactor, the yield of methanol increased from 2.4% (based on consumed methane) at 10% oxygen to 60% (based on consumed methane) at 0.6% oxygen. A study of the explosive oxidation of methane at 160 atm and 10% oxygen showed that the yield of methanol dropped from 9% methane consumed to less than 1% methane consumed when the initial temperature was increased from 100°C to 250°C.

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Newitt and Szego (10) studied the slow, high pressure oxidation of methane and related compounds in a flow system. Their results, summarized in Table 2, indicate that as much as 50% of the methane consumed is converted to methanol using low reaction times and low concentrations of oxygen. No formic acid was detected and the ratio of CO/CO_2 was approximately 1. The authors concluded that methanol was the initial product from the oxidation reaction. The conversion of methane to methanol at high pressures was optimal at 450°C.

In 1934 Wiezevich and Frolich (11) reported on their study of the direct oxidation of saturated hydrocarbons at high pressures in a flow system. These authors showed that the optimum pressure for production of methanol was 135 atm. They also showed that the flow rate did not have a significant effect on the yield of methanol. At 135 atm, the temperature for the onset of the oxidation reaction with methane was about 500°C. When the reaction was carried out with natural gas at 390°C, 135 atm and 5.4% oxygen content, as much as 30% of the condensed liquid was methanol. However, the total liquid product represented only a 3.7% yield in terms of reacted methane. Most of their experiments were done with natural gas containing about 2% ethane. When the ethane content in the inlet gas was increased to 12%, the yield of methanol in the liquid product increased from 14% to about 32%. Since the increased yield of methanol could not be accounted for by the increased amount of ethane present, it was concluded that the methanol was formed by oxidation of methane sensitized by the ethane present. Contrary to the conclusion of Pichler and Reder (9), these authors found that catalysts such as iron, nickel and aluminum tended to increase the yield of methanol.

Further work on the oxidation of methane and intermediate products has been reported by Norrish and Foord (13), Bone and Gardner (14) and Newitt and Gardner (15). These authors were primarily concerned with solving the dispute regarding the hydroxylation mechanism and the role of peroxides.

In 1937, Newitt reviewed much of the early work on high pressure oxidations of methane and other hydrocarbons (16). It was also in this year that Boomer and his students at the University of Alberta published three articles

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on the oxidation of methane at high pressures (17, 18, 19). Using natural gas containing 90% methane, 3.5% ethane and 5% nitrogen, they showed that copper was an effective catalyst in the formation of methanol in a high pressure flow-through system. Some typical results from Boomer's work are recorded in Table 3.

Boomer's work presents a number of interesting points. Firstly, the yield of methanol increased as the concentration of oxygen decreased. Secondly, the effect of flow rate was more pronounced at low oxygen concentrations than it was at high oxygen concentrations and only a slight increase in methanol yield was observed when the flow rate was decreased. Thirdly, these authors reported the detection of hydrogen which previously had only been observed in the explosion reaction. And fourthly, the copper catalyst was easily poisoned by traces of sulfur resulting in about 50% reduction of its normal catalytic value.

When methane containing 5.7% nitrogen was used as a reactant (19), much higher temperatures were required than those found necessary for natural gas. These results confirmed what had been found by Pichler and Reder (9) and by Wiezevich and Frolich (11). The lower temperatures required for reactions with natural gas were attributed to the presence of ethane and propane which underwent oxidation at lower temperatures than methane. Intermediates in the oxidation of ethane and propane presumably catalyze the overall oxidation of methane. At a pressure of 180 atm, temperature of 475°C, 3.2% oxygen and 16.78% nitrogen, the yield of methanol was 74% of the methane consumed with a flow rate of 0.84 liter per minute. Under these conditions the amount of methane consumed during the reaction was only 1.9%. A material balance for oxygen showed that 75% of the oxygen was accounted for in the products.

These results were similar to those observed by previous workers (9, 11). Figure 1 correlates the yield of methanol with the oxygen concentration at various pressures.

Boomer's results indicated that other catalysts, namely steel, silver and glass could also be used. All these three catalysts were found to be as

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effective as copper. However, since the reactor used was copper-plated, it was hard to distinguish between the exposed catalyst and the remaining part of the apparatus. Boomer and Naldrett (20) reported some interesting effects with regard to the form of the catalyst. Copper in the form of gauze was less effective than blocks of copper. The difference was attributed to the greater free space in the reaction zone. Comparison of nickel, zinc and silver gauzes showed that nickel was the most effective and zinc gauze the least effective in catalyzing the conversion of methane to methanol. Interestingly, nickel gauze was more effective than copper gauze. Experiments with Monel metal (a nickel-copper alloy) showed it to be highly effective as a catalyst. Boomer concluded from his work that to ascertain the commercial feasibility of the process a recycling system should be used so that high yields could be achieved under conditions of low conversion rates.

Russian workers started to study methanol formation in 1946 when Furman (21) reported on the high pressure oxidation of methane in a flow system. The results are summarized in Figures 2 and 3. Furman's results appear to contradict previous work (9, 19) which showed higher methanol yields at lower O_2 concentrations. Furman and Tsiklis (22) also studied the oxidation of methane under adiabatic compression. The reaction was reported to commence at 1200°K. Though formaldehyde was detected, no methanol was found. These authors also studied the oxidation reaction at 365-400°C and at 10 to 300 atm with air and oxygen.

More recently, Nalbandyan and coworkers (23) re-examined the oxidation of methane under adiabatic compression. Their results are shown in Figure 4. Other products analyzed for were H_2, C_2H_6, C_2H_4. C_2H_2 and C_3H_6. These products are shown as a function of compression ratio α in Figures 5 an 6. The authors concluded that the methanol and formaldehyde were formed by the following reactions:

$$CH_3O^{\bullet} + CH_4 \longrightarrow CH_3OH + CH_3^{\bullet} \qquad (4)$$

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$$CH_3^\bullet + O_2 \longrightarrow CH_3OO^\bullet \qquad (5)$$

$$CH_3OO^\bullet + CH_4 \longrightarrow CH_3OOH + CH_3^\bullet \qquad (6)$$

$$CH_3OOH \longrightarrow CH_3O^\bullet + {}^\bullet OH \qquad (7)$$

$$CH_3OO^\bullet \longrightarrow CH_2O + {}^\bullet OH \qquad (8)$$

The thermodynamics of the oxidation of alkanes to alcohols (24) showed that lower temperatures favoured alcohol formation.

The effect of HF treatment of the glass walls of reactors in static, low pressure systems (25) was to lower the rates of oxidation and to bring the methanol yields down to values closer to those of formaldehyde. The plot of $R_{CH_3OH}/R_{CH_2O}[CH_4]$ against 1/T gave an activation energy difference of about 20 kcal/mode for the two proposed reactions:

$$CH_3O^\bullet + CH_4 \xrightarrow{k_A} CH_3OH + CH_3^\bullet \qquad (9)$$

$$CH_3O^\bullet \xrightarrow{k_F} CH_2O^\bullet + H^\bullet \qquad E_F - E_A = 20 \text{ kcal/mole} \qquad (10)$$

Though much has been written about the effect of surfaces in the oxidation reactors on the conversion of methane to methanol (13, 26, 27, 28, 29, 30), very little has been reported concerning the effects of specific catalysts on the yield of methanol. The work of Boomer quoted earlier seems to be the single major contribution in the field (19, 20).

The spontaneous ignition of methane-air mixtures at high pressure was studied by Melvin in 1965 (31, 32). The activation energy for both the ignition delay and the rate of the slow reaction preceding the expolosion ranged from 39 to 45 kcal/mole. The products detected during the ignition delay included H_2, CO_2, methanol and formaldehyde together with minute amounts of ethane and ethylene. Carbon monoxide did not appear during the ignition delay time.

.../8

The reaction was studied at pressures from 58 to 110 atm and at an initial temperature of about 350°C. The activation energy for the reaction in the initial stage of the expolosion was 20 to 25 kcal/mole. Explosion products included relatively large amounts of hydrogen and ethane indicating the reaction mixture was dominated by hydrogen atoms. The hydrogen atoms were possibly formed by the following reaction:

$$^{\bullet}OH + CO \longrightarrow CO_2 + H^{\bullet} \qquad (11)$$

However, since hydrogen appears before carbon monoxide it is more probable that the following reaction is the initial source of the hydrogen atoms:

$$^{\bullet}OH + H_2 \longrightarrow H_2O + H^{\bullet} \qquad (12)$$

The partial oxidation of methane at pressure up to 13,000 atm (200,000 psi) was studied in a static system by Lott whose Ph.D. Thesis (33) constitutes an excellent review of the subject to 1965. At 3500 atm (50,000 psi) and an initial temperature of 262°C the yield of methanol was 40% for a residence time of about 10 minutes. The methane reacted was 6.3% whereas the oxygen consumed was 95.2%. Other products analyzed for were formic acid, formaldehyde and methylformate, as well as CO and CO_2. Cool flame phenomenon was observed at 3300 atm (48,000 psi) and 262°C. A portion of Lott's thesis has been published (34).

At this time Knox reviewed the low temperature oxidation of hydrocarbons in the gas phase (35, 36). Hoare and co-workers also reported on the relative rates of reaction of OH radical with methane and various intermediates. The formation of methanol was not reported (37).

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The low temperature, low pressure oxidation of hydrocarbons has been summarized by Antonik and Lucquin (38) who, by means of four interrelated mechanisms, attempted to account for explosion, cool flame and slow oxidation reactions. The same authors studied (39) the oxidation of methane at 44°C and 700 Torr. They showed that methanol, formaldehyde and hydrogen peroxide all pass through maxima at between 5 and 10 minutes reaction time. In the presence of 0.2% hydrogen bromide the maxima shifts down to 2 minutes of reaction time with the absolute amount depending on the methane/oxygen ratio.

The partial oxidation of methane in a flow system at atmospheric pressure and over a temperature range of 450 to 700°C was studied under a variety of conditions (40). Though formaldehyde and hydrogen peroxide were detected the production of methanol was not reported (41).

The oxidation of methane in the presence of small concentrations of chlorine representing from 0.2 to 0.8% of the reaction mixture showed a decrease in the induction period of the reaction at 440°C and 700 Torr for stoichiometric oxygen-methane mixtures. In general, the yields of methanol and hydrogen peroxide were larger in the absence of chlorine whereas formaldehyde was unaffected by chlorine at high methane concentrations and increased in the presence of chlorine at lower methane concentrations. The formation of performic acid was considered a key step in the oxidation process (42).

The oxidation of methane in a static system at 700 Torr and in stoichiometric methane-oxygen mixtures has been studied (43). The yield of methanol as a function of reaction temperature and time was examined over the temperature range of 400 to 472°C. The methanol yield as a function of reaction time passed through a maximum which increased and broadened as the temperature decreased. The effect of pressure on the methanol yield was studied at 445°C using the same stoichiometric methane-oxygen mixture. As the pressure dropped from 700 Torr to 200 Torr the maximum in the yield of methanol dropped and shifted to longer reaction time. The results were interpreted in terms of reaction mechanisms which had previously been proposed and which included the performic acid radical.

.../10

The French workers have extended their studies (44) to include a recirculating system for the oxidation of methane as well as a study of the effect of N_2 and NO on the reactions. Increasing NO (0.5 to .5%) in a static system at 620°C showed a slight increase in the maximum rate of formation of formaldehyde (0.9 to 1.25%) but the yield based on CH_4 consumed decreased (22.5 to 15.5%). The effect of NO on methanol formation was not reported. Nitrogen (12 - 63%) increased the yields of CH_2O (7 to 10.5%) as well as its maximum rate of formation (.55 to .80%).

A study of the high pressure, static oxidation of methane was reported for the pressure range of 1700 to 3400 atm using a mixture of 92% methane and 8% oxygen (45). Products analyzed for were carbon monoxide, carbon dioxide, formalydehyde, water, methanol, ethanol and formic acid. Hydrogen and hydrogen peroxide were not detected. In some cases small quantities of acetone were found in the liquid product. The temperature range covered in this study was from 270 to 480°C with residence times of approximately 30 minutes. At 290°C and 1700 atm all products increased with an increase in residence time from 15 to 60 minutes. The water and carbon dioxide seemed to show the most pronounced effect.

A study (46) of the formation of methanol during the gas phase oxidation of methane at 456°C in a static system under atmospheric conditions was reported for the methane-oxygen ratios of 9/1, 4/1 and 2/1. Maximum methanol yields of about 20% were obtained for reaction times of 200 and 300 seconds in the cases of the 4/1 and 9/1 ratios. The 2/1 mixture gave a maximum methanol yield of approximately 12% at a reaction time of 200 secs.

The additional reaction schemes proposed to account for the results are as follows:

$$2\ CH_3O_2^{\bullet} \longrightarrow 2\ CH_3O^{\bullet} + O_2 \qquad (13)$$

$$2\ CH_3O^{\bullet} \longrightarrow CH_3OH + CH_2O + O_2 \qquad (14)$$

$$CH_3O^{\bullet} + O_2 \longrightarrow CH_2O + HO_2^{\bullet} \qquad (15)$$

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$$CH_3O^{\bullet} + CH_4 \longrightarrow CH_3OH + CH_3^{\bullet} \qquad (16)$$

$$CH_3O^{\bullet} + CH_2O \longrightarrow CH_3OH + CHO^{\bullet} \qquad (17)$$

$$CH_3O^{\bullet} + M \longrightarrow CH_2O + H^{\bullet} + M^{\bullet} \qquad (18)$$

In a series of six papers, Karmilova, Enikalopyan and Nalbandyan (47 to 52) have examined the kinetics and mechanism of methane oxidation. Stoichiometric ratios of CH_4 to O_2 were used at sub-atmospheric pressures over the temperature range of 423-513°C. Products reported were CO, CO_2, H_2, H_2O_2, H_2O, CH_2O, CH_3OH. The introduction period had an activation energy of 36 kcal/mole -- about 7 kcal/mole less than that of the consumption of CH_4. Maximum yields of hydrogen peroxide were similar to those of CH_2O -- the ratio of H_2O_2/CH_2O being 1.6 at 400°C and 0.4 at 500°C. The H_2O_2 was believed to form from the CH_2O which had an activation energy of formation of 7.8 kcal/mole.

Based on the following reaction scheme the authors (49) showed an excellent agreement between the calculated and experimental kinetic parameters.

$$CH_4 + O_2 \longrightarrow CH_3^{\bullet} + HO_2^{\bullet} \qquad (19)$$

$$CH_3^{\bullet} + O_2 \longrightarrow CH_2O + {}^{\bullet}OH \qquad (20)$$

$$CH_4 + {}^{\bullet}OH \longrightarrow CH_3^{\bullet} + H_2O \qquad (21)$$

$$CH_2O + {}^{\bullet}OH \longrightarrow HCO^{\bullet} + H_2O \qquad (22)$$

$$CH_2O + O_2 \longrightarrow HCO^{\bullet} + HO_2^{\bullet} \qquad (23)$$

$$HCO^{\bullet} + O_2 \longrightarrow CO + HO_2^{\bullet} \qquad (24)$$

$$CH_4 + HO_2^{\bullet} \longrightarrow CH_3^{\bullet} + H_2O_2 \qquad (25)$$

$$HO_2^{\bullet} + CH_2O \longrightarrow H_2O_2 + HCO^{\bullet} \qquad (26)$$

..../12

The effect of H_2O_2 (0.1 - 0.4%) and H_2O on the reaction kinetics was studied at 423 to 491°C. The H_2O_2 decreased the induction period as the formation of OH starts the chain reaction via:

$$CH_4 + {}^{\bullet}OH \longrightarrow CH_3{}^{\bullet} + H_2O \qquad (27)$$

Water (up to 6%) had no effect on the induction period at the higher temperatures (472 to 513°C). However, at lower temperatures a slight effect was was noted. The reaction

$$CO + {}^{\bullet}OH \longrightarrow CO_2 + H^{\bullet} \qquad (28)$$

was proposed (51, 52) as an important step accounting for CO_2 formation.

Kogawa and Lunsford (53) reported a new process for the oxidation of methane to get high yields of methanol and formaldehyde using N_2O as an oxidant. The MoO_3/SiO_2 catalyst for the process was prepared by the equilibrium adsorption method from an aqueous solution of $(NH_4)_6Mo_7O_{24}$ at a pH of 11.

It gave 26% conversion to methanol at 500°C and a total selectivity of 95% to methanol and formaldehyde. The O^- radical from N_2O is considered to promote the oxidation of methane.

Although there is as yet no economical way to accomplish the synthesis commercially, the initial results are encouraging. The use of nitrous oxide as an oxidant may have to be replaced by a cheaper source of oxygen to make the process economically feasible (54).

Commercial interest in the conversion of methanol to formaldehyde is well established. Two patents (55, 56) have been issued for the controlled oxidation of methane to methanol-formaldehyde mixtures. Brockhaus obtained high yields (H_2CO = 47.5% and CH_3OH = 71.1%) with up to 45% conversion of methane were obtained by a high pressure (8-60 atm) flame with a residence time of 1.08×10^{-3} to 1.76×10^{-3} sec. The H_2CO and CH_3OH produced were dissolved in water.

.../13

When oxygen was used instead of air the 60-80% CH_4 in the waste gas was recycled. The second patent (56) describes a thermal oxidation at 300 to 600°C at 5 atm with velocities of 1-15 m/s for CH_4 and 75-250 m/s for O_2. Combined yields of 91% for H_2CO and CH_3OH were obtained.

Recently Koenig (57) of Wesseling, W. Germany has revealed in a patent application (DOS 3.101.024 - 1982) that methane could be converted to methanol with 92% selectivity in the liquid phase (aqueous solution of $Fe_2(SO_4)_3$, pH = 1.0) using Pd-Ag-alloy (0.6 wt %) on graphite. Optimal reaction conditions are: T=20-30°C, P=30-60 bar. The reoxidation of Fe^{II} to Fe^{III} is conducted in a separate reactor with air at 130-170°C and 6-10 bar pressure.

The references of general texts on the oxidation reactions of hydrocarbons are included (58-63).

(a) Effect of temperature, pressure, oxygen concentration and residence time:

Based on the available data from some of the references cited in this review, the effect of reaction conditions on methanol yield is summarized in Table 4. The wide range of operating conditions employed by various researchers provide only a general trend from this comparison. Within the range of the variables reported in Table 4, the conversion of methane to methanol is favoured by high pressure, high temperature and low oxygen concentration. The residence time, which primarily depended on the experimental system used, does not seem to have a significant effect on methanol yield.

(b) Effect of catalysts and presence of higher hydrocarbons:

The metal surfaces such as nickel, copper, silver, steel and certain alloys seem to have a catalytic effect on the oxidation reaction of methane to methanol. A systematic study to ascertain the effect of various catalysts on methanol yield will be of considerable value.

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Presence of higher hydrocarbons specially ethane in small quantities seems to have a favourable influence on the oxidation of methane to methanol. However, the exact mechanism by which ethane improves the methanol yield has not been investigated. The finding will be of special interest for oxidation processes in which natural gas instead of methane is used as a feedstock for methanol production.

NEED FOR FUTURE WORK

Most of the work on the oxidation of methane performed in the past was aimed at elucidating the reaction mechanism during oxidation. It was of special interest at that time since free radicals had just been introduced as reactant intermediates in oxidation and decomposition reaction. Obviously no effort was made to optimize the production of methanol.

In the new context of alternative transportation fuels (64, 65), the direct oxidation reaction of methane should be examined as a process to commercially produce methanol. Future work in this area should therefore address all aspects for optimizing methanol production. This would include the determination of optimum operating conditions (pressure, temperature, residence time, CH_4/O_2 ratios); effect of the presence of other hydrocarbons (ethane, propane etc); and the catalytic effect of various substances. Research should also be directed toward improving product selectivity. The presence of an easily abstractable hydrogen greatly increases the yield of methanol from the methoxy radical. The energetics of the various intermediate reactions would help locate optimum conditions for methanol conversion.

An experimental study of direct oxidation of methane to methanol under progress at the University of Manitoba is expected to answer some of these important questions.

ACKNOWLEDGMENT

The authors express their thanks to Julie Silins for her assistance in a thorough literature search.

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TABLE 1.

The Effect of Temperature upon the Survival of Methyl Alcohol and Formaldehyde in the Products of Methane Oxidation at High Pressures (8).

Initial Mixture, CH_4/O_2 = 8.1/1.

Initial Temp. °C	Rise in Temp. °C	Duration of - Induction (mins)	Duration of - Reaction (mins)	Ratio CO/CO_2 in gaseous products	Survival as % Methane Burnt CH_3OH	Survival as % Methane Burnt HCHO	Ratio $CH_3OH/HCHO$
Initial Pressure = 48.2 atm							
360	7	14	12	0.28	3.2	0.5	6.4
367	7	7	8	0.04	5.2	0.5	10.4
370	9	5	4	0.15	11.2	0.7	16.0
373	12	1.5	4	0.21	13.7	0.7	19.6
Initial Pressure = 106.4 atm							
336	4	53	35	0.05	10.1	0.30	33.6
339	10	14	22	0.01	14.1	0.36	39.2
341	14	2.5	9.5	1.5	22.3	0.75	29.4
343	10	--	12	1.0	20.0	0.93	21.5
Initial Pressure = 150 atm							
335	13	14	33	1.04	11.9	0.3	39.6
341	17	5	11	0.06	19.0	0.6	31.6
343	32	--	instan-taneous	2.1	21.1	0.4	52.7

TABLE 2.

Yield of Methanol and Formaldehyde from the Oxidation of Methane in a Flow System at 50 atm (10).

	Initial Mixture		Initial Temp. of Reaction Tube °C	Rise of Temp. °C	Duration of Heating secs.	Percentage of Methane burnt surviving as: CH_3OH	HCHO
(1)	CH_4	90	430	5	5	51	4.1
	O_2	3	430	5	7	49	3.2
			410	15	10	43	3.2
	N_2	7	400	28	20	12	2.16
(2)	CH_4	90	410	35	5	29.0	1.4
	O_2	5	410	46	7	18.0	0.9
	N_2	5	400	75	30	3.0	1.0

TABLE 3.

Experiments at a Pressure of 185 atm, showing the Effect of Temperature, Rate of Flow and Oxygen Concentrations on Yields (Boomer et. al.)

Experiment No.	86	67	58	77	80	81	79	85	91
Temperature, °C	325	350	350	350	350	350	350	400	425
Off-gas Flow (L/min.)	0.95	0.86	0.80	0.78	1.0	1.04	1.30	0.94	1.00
In-gas Analysis									
O_2	4.1	8.45	12.0	3.76	3.68	3.66	3.73	3.71	3.68
CH_4	72.2	54.0	38.8	76.4	75.3	75.4	75.3	73.8	77.1
C_2H_6	2.76	1.79	1.21	1.88	2.42	2.63	2.66	2.03	2.0
N_2	20.94	35.76	47.99	17.96	18.6	18.31	18.31	19.88	17.2
Off-gas Analysis									
CO_2	0.58	1.76	3.31	0.61	1.07	0.95	2.45	0.53	0.42
O_2	0.0	0.74	0.65	0.32	0.21	0.21	0.5	0.0	0.0
H_2	0.63	0.82	1.17	0.47	0.42	0.53	0.5	0.53	-
CO	0.63	2.57	2.11	1.21	1.08	1.24	1.21	0.53	-
CH_4	74.9	55.8	40.1	77.8	78.5	77.6	75.0	75.1	-
C_2H_6	1.81	0.31	0.1	1.1	0.81	1.5	1.48	2.68	-
N_2	21.45	38.0	52.6	18.49	17.9	17.97	18.86	20.63	-
Volume in-gas / Volume out-gas	1.03	1.08	1.14	1.04	1.04	1.04	1.03	1.05	1.00
Condensate, g/100 L in-gas at N.T.P.									
CH_3OH	2.20	2.06	1.37	1.73	1.60	1.72	1.83	1.97	2.06
CH_2O	0.194	0.159	0.114	0.198	0.166	0.151	0.185	0.198	0.094
HCOOH	0.063	0.063	0.016	0.031	0.037	0.040	0.033	0.02	0.01
H_2O	2.90	6.32	3.64	2.46	2.76	2.35	2.11	2.66	3.15
Alcohol in Condensate%	41.0	23.9	13.5	39.0	35.1	40.3	44.0	40.6	38.8
Total Carbon Oxidized%	3.73	9.73	14.2	3.92	4.16	4.31	6.17	3.24	-
Yields, as % of total carbon burned to:									
CH_3OH	53.3	25.9	16.5	38.8	33.8	34.6	25.8	54.3	-
CH_2O	5.02	2.12	1.46	4.75	3.72	3.25	2.77	5.75	-
HCOOH	1.06	0.51	0.14	0.48	0.54	0.57	0.32	0.37	-
Total	59.38	28.54	18.1	44.03	38.06	38.32	28.9	60.42	-
Total Inlet Oxygen accounted for,%	87.0	95.0	86.3	99.0	111.0	105.0	146.0	87.0	-

TABLE 4.

Summary of Methane to Methanol Conversion

Reference	Operating Temp.Range °C	Operating Press.Range atm	Residence Time min.	Oxygen Cons. %	Methanol yield %	Remarks
Richler & Reder (9)	350°	160		10	14.8	Static System
	500°	100	0.17	10 - 0.6	2.4-60	Flow System
	100°-250°	160		10	9 - 1	Explosive Oxidation
Newitt & Szego (10)	400°-430°	50	0.08-0.5	3 - 5	51.0 max	
Wiezerich & Frolich (11)	390°-500°	135		5.4	3.7	Flow System
Boomer et.al. (17,18,19)	325°-425°	185		3.66-12.0	16 - 54	
Lott (33,34)	262°	3500	10		40	
Luckett & Mile (46)	456°	1	3-5	10 - 50	12 - 20	Static System

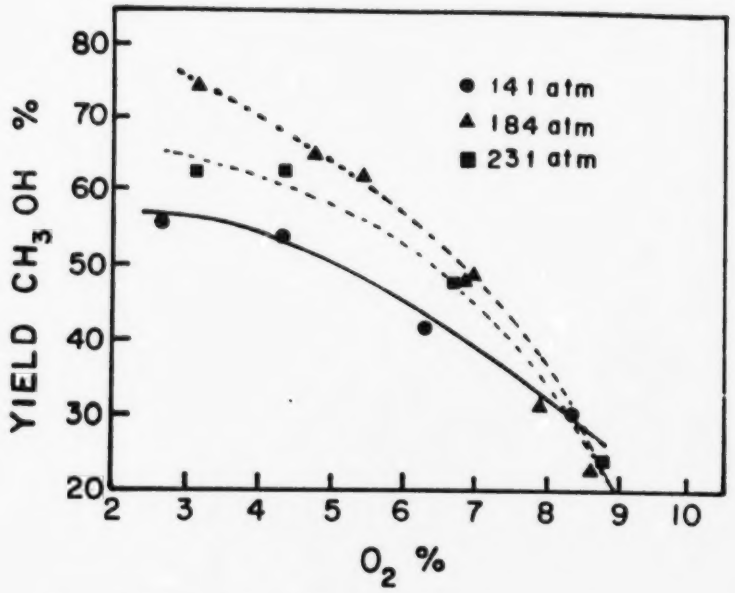


FIGURE 1. (Ref.19)

Methanol yield as a function of pressure and O_2 concentration.

FIGURE 2. (Ref.21)

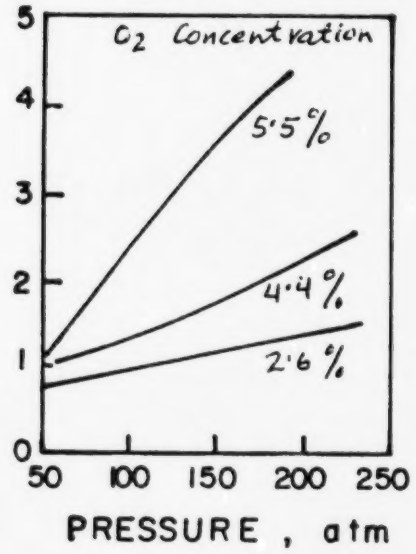
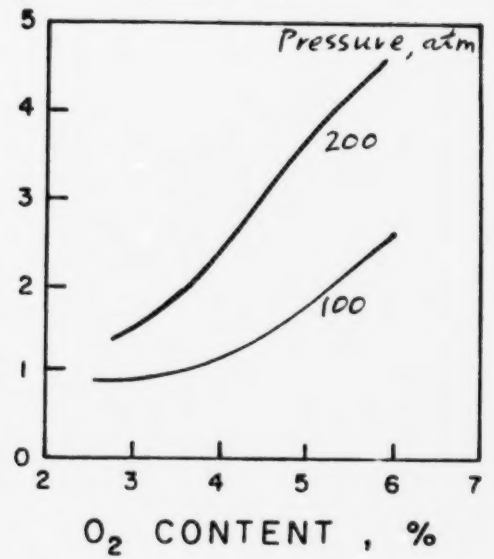


FIGURE 3. (Ref.21)



Methane to methanol conversion at 400 °C and 50 lit/h gas flow.

w = gm of methanol/100 lit of gas.

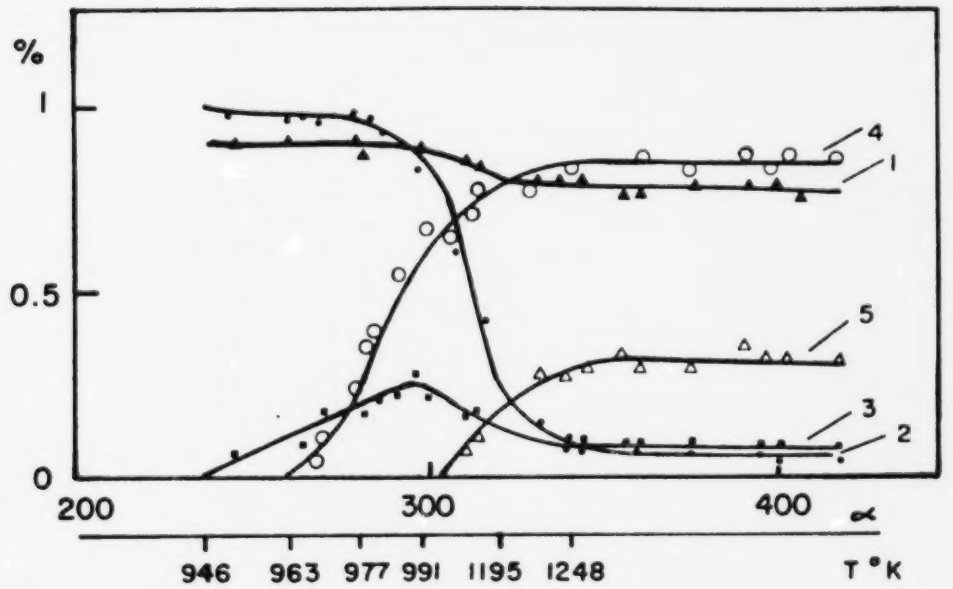
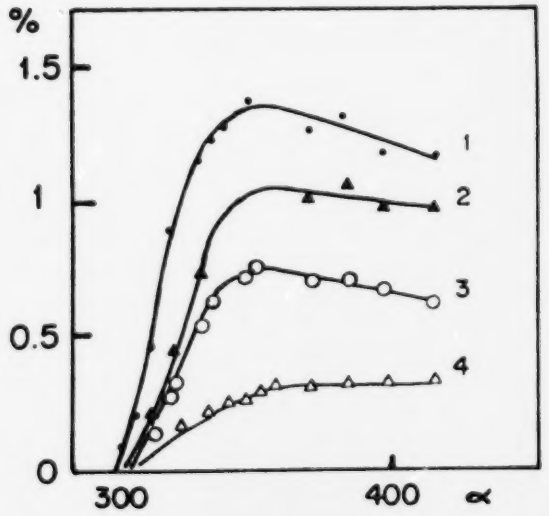


FIGURE 4. (Ref.23)

Yield of products as a function of Compression Ratio α.

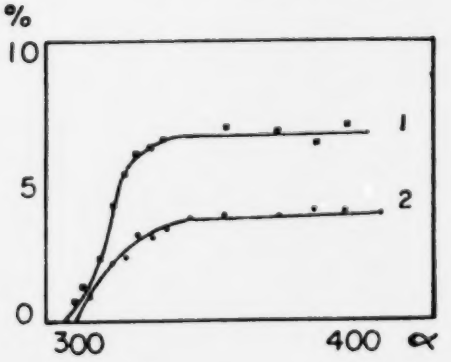
1 - $CH_4 \times 10^{-2}$
2 - $O_2 \times 10^{-1}$
3 - CH_3O
4 - CH_3OH
5 - $C_2H_5OH \times 10$

FIGURE 6. (Ref.23)



Yield of (1) C_2H_6 (2) C_2H_4 (3) C_2H_2 and (4) $C_3H_6 \times 10$ as a function of Compression Ratio α .

FIGURE 5. (Ref.23)



Yield of (1) CO and (2) H_2 as a function of Compression Ratio α .